

Design of continuous crystallization processes

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Abstract

Crystallization is an efficient thermal separation technology with low operational costs, which provides a sophisticated opportunity for purification together with the adjustment of the final product crystal size distribution (CSD). The continuous operation of the corresponding application is of interest when a large space-time-yield and constant output specifications are demanded. Nevertheless, the commonly preferred batch operation is usually simpler with respect to process design and set-up. Here, e.g. seed crystals can be utilized together with controlled cooling policies to efficiently control the final CSD. In case of a continuous process, these properties have to be adjusted by the basic crystallization mechanisms, i.e. nucleation, growth and dissolution. These mechanisms are connected to the operation conditions in a nonlinear way, which complicates the transfer of the existing batch to continuous processes. Therefore, the design of continuously operated crystallizations from solution will be the main topic of the present thesis and the following tasks will be investigated.

Besides mass balances also population balances (PBE) have to be considered for crystallization processes to capture the evolution of the solid phase. However, these PBEs contain mathematical sub-models for the relevant kinetic phenomena, which have to be quantified expensively in separate experiments for every new substance system or even for the specific experimental set-up. Hence, an efficient and universally applicable quantification method for the estimation of crystallization kinetics would be beneficial as well as the evaluation of the design of a continuous process based on these information. Consequently, a subsequent evaluation of the impact of the so quantified kinetics, e.g. the utilized mathematical approach and measurement errors, on the process design is necessary as well.

Nevertheless, complicated separation problems, like enantiomeric mixtures or substance systems with miscibility in the solid state, exist. In such cases product purity is of main interest. Fractional crystallization is one option to purify mixtures, which form solid solutions, by repeated successive steps. Nevertheless, the necessary and repetitive solid-liquid separation and the difficult solid phase transport between the corresponding crystallizations are expensive and the lack of a supporting mathematical framework complicates process design.

Therefore, the present thesis is divided into two main parts:

For the model-based design, control and optimization of crystallization processes a novel method for the estimation of the relevant kinetics is developed. This short-cut-method is based on analyzing the evolution of the crystal size distribution during a few well-planned polythermal experiments. The required information are subsequently extracted from a characteristic part of the particle collective, which allows a sequential

and therefore efficient quantification of the different kinetics. The feasibility of this method is demonstrated on the basis of systematic theoretical and experimental studies. Subsequently, three different binary substance systems are characterized with respect to their kinetics. The information of one of these is then applied for the design of a continuous process.

The second main part focuses on an innovative fractional counter-current crystallization process. The disadvantages mentioned above are avoided by means of repeated crystallization and dissolution to transport the solid phase in the dissolved, liquid state. Hence, a pseudo-continuous automated process is feasible similar to simulated moving bed chromatography or mixer-settler plants for extraction. The application of this process for substance systems exhibiting partial or total solid solutions is shown in theory and experiment. A supporting model is derived, which allows process visualization, design and optimization. This sophisticated approach consists of a simple stage-model, which comprises the data of the ternary solid-liquid equilibria. The results of this study concern the demonstration of the process principle for two selected ternary systems, which are characterized by complete miscibility in the solid state. Subsequently, the scale-up from a laboratory unit to a pilot plant with the verified model is shown. Finally, a theoretical evaluation of the feasibility of the process principle for purification of systems characterized by partial miscibility in the solid state is given.

Kurzzusammenfassung

Kristallisation ist eine effiziente und kostengünstige thermische Trennmethode, die neben der Aufreinigung auch die Möglichkeit bietet, die Produktqualität und hier im Speziellen die finale Kristallgrößenverteilung (KGV) einzustellen. Wie auch in der chemischen Reaktionstechnik sind dabei vor allem kontinuierliche Prozesse von Interesse welche eine hohe Raum-Zeit-Ausbeute bieten. Die Umstellung der momentan präferiert absatzweise betriebenen Kristallisationen stellt jedoch eine große Herausforderung dar, da neben der stofflichen Bilanzierung vor allem die partikuläre Phase von entscheidender Bedeutung ist. Die Möglichkeit, zum Beispiel über Impfkristalle die KGV des Produktes effektiv steuern zu können, entfällt bei der kontinuierlichen Betriebsweise. Dieses Kriterium muss in diesem Fall über die Hauptmechanismen der Kristallisation, unter anderem Nukleation, Wachstum und Auflösung, eingestellt werden. Diese sind jedoch komplex und nichtlinear mit dem Stoffsystem, dem Reaktoraufbau oder auch mit den gewählten Betriebsbedingungen, wie zum Beispiel Temperatur und Verweilzeit, verknüpft. Daraus ergeben sich die Fragestellungen dieser Arbeit, welche sich vor allem mit der Kristallisation aus wässrigen Lösungen beschäftigt.

Die Einstellung der KGV setzt inhärent Informationen über die Kinetiken der Nukleation, des Wachstums und der Auflösung voraus, die bisweilen aufwendig in separaten Experimenten, für jedes neue Stoffsystem oder jeden neuen Prozessaufbau, bestimmt werden müssen. Des Weiteren ist zu bewerten, wie sich die Kinetiken, d. h. der gewählte mathematische Ansatz, die darin enthaltenen quantifizierten Parameter, sowie evtl. Messfehler bei der Kinetikbestimmung, auf die kontinuierliche Prozessführung auswirken.

Auf der anderen Seite lassen sich spezielle Trennprobleme, nicht durch eine einzelne Trennstufe, unabhängig von der Fahrweise, lösen. Hierzu zählen unter anderem Stoffsysteme welche sogenannte feste Lösungen bilden. In einem solchen Fall, kommen kaskadierte Prozesse, wie zum Beispiel die fraktionierte Kristallisation, zum Einsatz, die durch wiederholtes Kristallisieren, abhängig von den charakteristischen thermodynamischen Eigenschaften des Stoffsystems, eine schrittweise Anreicherung erzielen. Die dabei benötigte, repetitive fest-flüssig Trennung als auch der Feststofftransport zwischen den Stufen stellen dabei allerdings einen wirtschaftlichen Nachteil dar und fehlende detaillierte Prozessmodelle erschweren die zielgerichtete Auslegung solcher Kristallisationskaskaden.

Die Arbeit gliedert sich in zwei Hauptteile:

Für die modelbasierte Auslegung der kontinuierlichen Betriebsweise soll eine neuentwickelte Methode zur Kinetikbestimmung untersucht werden. Die

Herangehensweise fußt dabei auf der Analyse der Entwicklung der KGV während möglichst weniger, polytroper, absatzweiser Kristallisationen. Die benötigten Informationen werden aus einem charakteristischen Teil des Partikelkollektivs für die jeweiligen Mechanismen extrahiert, um so eine effektive sequentielle Parameterschätzung zu ermöglichen. Die Funktionalität der vorgeschlagenen Methode wird dabei systematisch, anhand von theoretischen und experimentellen Studien, belegt. Abschließend werden die für ein binäres Stoffsystem bestimmten Kinetiken zur Auslegung und Analyse einer kontinuierlichen Kristallisation nach dem „mixed-suspension, mixed-product-removal“-Prinzip angewandt, um die Übertragbarkeit der quantifizierten Kristallisationsraten auf einen solchen Prozess zu bewerten.

Der zweite Hauptteil betrachtet einen neuartigen fraktionierten Gegenstromkristallisationsprozess. Die erwähnten Nachteile dieser Betriebsart werden dabei durch periodisches Kristallisieren und Auflösen vermieden welches eine semi-kontinuierliche Fahrweise, ähnlich der von „simulated moving bed“- oder „Mixer-settler“-Anlagen, ermöglicht. Die Anwendbarkeit dieses Prozesses auf ternäre Stoffsysteme, welche partiell oder über den kompletten Bereich der verschiedenen Zusammensetzungen feste Lösungen bilden, wird theoretisch und experimentell belegt. Zur Prozessbeschreibung wird ein Zellenmodell, basierend auf den thermodynamischen Charakteristika solcher Stoffsysteme, entwickelt und gemeinsam mit den vermessenen Gleichgewichtsdaten zweier ternärer, wässriger Salzsysteme verwendet. Das anhand von Vorversuchen validierte Modell dient anschließend zur erfolgreichen Auslegung von Experimenten im Pilotmaßstab.

Preface

Several publications were prepared in the course of this thesis and are therefore incorporated in the present manuscript. The chapters, which contain to some extent parts of these publications of the author, are listed in the following for the sake of clarity. Additionally, several students will be listed here as well, to acknowledge their assistance during the experimental works of the present thesis.

- Parts of chapter 5 were taken from [1].
- Parts of chapter 6 were taken from [2]. Experimental support was provided by M.Sc. N. Hoyer and M.Sc. U. Grobleben during their Master- and Bachelor-thesis.
- Experimental support for chapter 7 was provided by M.Sc. L. Wiczorek, during her Bachelor-thesis.
- Parts of chapter 8 were taken from [3] and [4].
- Parts of chapter 9 were taken from [3]. Experimental support was provided by Dipl.-Ing. S. Wloch, during a Diploma- thesis.

[1] Temmel, E.; Eisenschmidt, H.; Lorenz, H.; Seidel-Morgenstern, A., "A short-cut-method for the quantification of crystallization kinetics - Part 1: Method development" (*ready for submission*).

[2] Temmel, E.; Eicke, M.; Lorenz, H.; Seidel-Morgenstern, A., "A short-cut-method for the quantification of crystallization kinetics - Part 2: Experimental application" (*ready for submission*).

[3] Temmel, E.; Wloch, S.; Müller, U.; Grawe, D.; Eilers, R.; Lorenz, H.; Seidel-Morgenstern, A., "Separation of systems forming solid solutions using counter-current crystallization", *Chemical Engineering Science*, vol. 104, pp. 662-673, 2013.

[4] Temmel E.; Müller, U.; Grawe, D.; Eilers, R.; Lorenz, H.; Seidel-Morgenstern, A., "Equilibrium Model of a Continuous Crystallization Process for Separation of Substances Exhibiting Solid Solutions", *Chemical Engineering & Technology*, vol. 35, no. 6, pp. 980-985, 2012.

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